

First-Principles Insight into a Ru-Doped SnS₂ Monolayer as a Promising Biosensor for Exhale Gas Analysis

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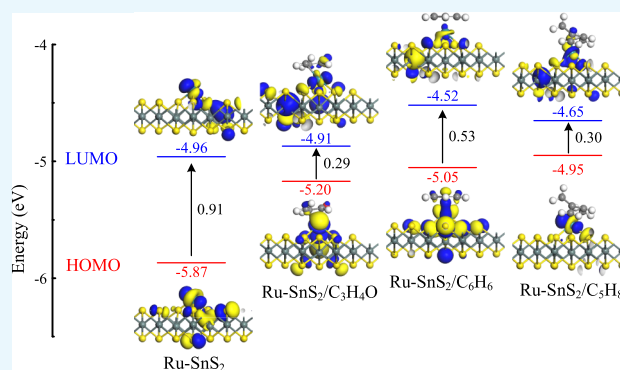
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ABSTRACT: Realizing the diagnosis of lung cancer at an inchoate stage is significant to get valuable time to conduct curative surgery. In this work, we relied on a density functional theory (DFT)-proposed Ru–SnS₂ monolayer as a novel, promising biosensor for lung cancer diagnosis through exhaled gas analysis. The results indicated that the Ru–SnS₂ monolayer has admirable adsorption performance for three typical volatile organic compounds (VOCs) of lung cancer patients, which therefore results in a remarkable change in the electronic behavior of the Ru-doped surface. As a consequence, the conductivity of the Ru–SnS₂ monolayer increases after gas adsorption based on frontier molecular orbital theory. This provides the possibility to explore the Ru–SnS₂ monolayer as a biosensor for lung cancer diagnosis at an early stage. In addition, the desorption behavior of three VOCs from the Ru–SnS₂ surface is studied as well. Our calculations aim at proposing novel sensing nanomaterials for experimentalists to facilitate the progress in lung cancer prognosis.



1. INTRODUCTION

As one of the commonest cancers in our human, lung cancer has received great attention in recent years given its high incidence and mortality rates.^{1,2} At present, bold proteomic patterns, nuclear magnetic resonance, and chest tomography are widely applied technologies for the diagnosis of lung cancer.^{3,4} However, these methods are somewhat time-consuming, expensive, or invasive and what is worse is that lung cancer in most cases can only be diagnosed at an advanced stage. In other words, these so-called progressive methods cannot effectively increase the survival rate of lung cancer.

To realize the diagnosis of lung cancer at an early stage, exhaled breath analysis, based on analyzing the exhaled gas of a possible patient daily, is proposed aiming at improving the whole survival.^{5,6} As reported, human exhaled gas contains more than 200 volatile organic compounds (VOCs), which can reflect the potential dysfunction of human organs.^{7,8} VOCs that are recognized as lung cancer biomarkers are hydrocarbons such as isoprene (C₅H₈) and methyl cyclopentane (C₆H₁₂), hydrocarbon derivatives such as 1-propanol (C₃H₈O) and 2-propenal (C₃H₄O) as well as aromatic hydrocarbons such as benzene (C₆H₆) and styrene (C₈H₈).^{3,9} That is, if the existence of these typical gases can be detected, the subjects are possible victims of lung cancer. To this end, surface-enhanced Raman spectroscopy was reported as a good candidate for the detection of VOCs. Apart from that, chemical resistance-type sensors with high sensitivity and

rapid response^{10–12} could also be a prospective method for the diagnosis of lung cancer through exhaled breath analysis. The sensing mechanism of such a sensor is based on the change in the conductivity of the sensing material after interaction with targeted gases.¹³ During the gas interaction, electrons will transfer between the adsorbent surface and gas molecules, changing the carrier concentration of the sensor and therefore modifying its electronic behavior.¹⁴ In fact, some scholars have proposed the application of resistivity-type sensors as promising devices in this field as it definitely provides a quite easy manner for the early diagnosis of lung cancer without pain and invasion.^{5,15} From this aspect, the materials with desirable chemical reactivity and high carrier mobility would be on priority to be exploited as potential sensors for VOCs.

Transition-metal dichalcogenides (TMDs) very recently become the focus of attention for sensing applications due to their strong chemical reactivity and high carrier mobility, especially when they are in two-dimensional (2D) structures. Among them, monolayer MoX₂ (X = S, Se, and Te) are first explored and reported to have strong potential for gas sensing

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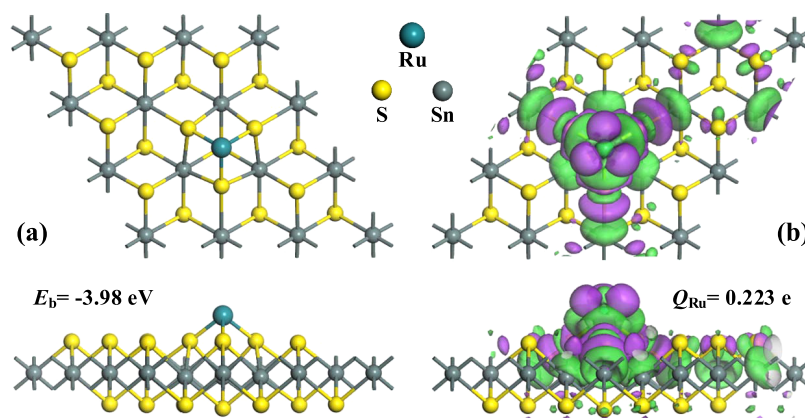


Figure 1. Geometric structure (a) and EDD (b) of the Ru–SnS₂ monolayer. In EDD, the green (purple) areas denote electron accumulation (depletion); the isosurface is set to 0.008 e/Å³.

applications.^{16–18} However, a SnS₂ monolayer that has a similar structure and property to those of a MoS₂ monolayer faces a lack of attention. In fact, the SnS₂ monolayer has an admirable indirect semiconducting property with a band gap of 2.60 eV¹⁹ and a superior carrier mobility of 50 cm²·V^{−1}·s^{−1},^{20,20} which confers its application for gas sensors, lithium-ion batteries, and water splitting.^{21–23} Moreover, through n-doping or p-doping of the SnS₂ monolayer, much more desirable properties could be obtained.²⁴ Ma et al.²⁵ reported a Pd-doped SnS₂ monolayer for gas sensing in transformer oil, which reveals the good performance of a transition-metal-doped SnS₂ monolayer as a gas sensor. Moreover, it also stimulates us to utilize a Ru-doped SnS₂ (Ru–SnS₂) monolayer for VOC sensing to exploit its potential in lung cancer diagnosis. The Ru dopant has been demonstrated with good catalytic behavior for gas interaction²⁵ and we believe that it can bring expected performance in VOC sensing. All of the reported results, including the optimization of the Ru–SnS₂ monolayer and the adsorption process, were obtained using the density functional theory (DFT) method. Our theoretical calculations can provide the sensing mechanism of the Ru–SnS₂ monolayer, and with the successful synthesis of large-scale atomic-layer SnS₂,^{26,27} we are hopeful that the Ru–SnS₂ monolayer could be explored as a novel chemical gas sensor in many fields.

2. RESULTS AND DISCUSSION

2.1. Ru Doping Behavior on the SnS₂ Monolayer. We defined the adsorption of one Ru dopant on the pristine SnS₂ monolayer to form a Ru–SnS₂ counterpart. The parameter of binding energy (E_b) was used to evaluate the chemical stability of the Ru–SnS₂ monolayer, the E_b is calculated by the energy of Ru–SnS₂ subtracting the total energies of pristine SnS₂ and the Ru atom. Three doping sites were considered, namely, T_{S1} (on top of the S atom of the first layer), T_{Sn} (on top of the Sn atom of the second layer), and T_{S2} (on top of the S atom of the second layer). After full optimization, the most stable configuration for Ru doping is through the T_{S1} site, which possesses lower E_b compared with that of the T_{Sn} site. Interestingly, after the optimization of Ru doping on the T_{S2} site, the Ru dopant experiences somewhat displacement, making the structure the same as that of the T_{S1} site. Figure 1 plots the geometric structure and electron deformation density (EDD) of the identified Ru–SnS₂ monolayer.

As shown in Figure 1a, the E_b of the Ru–SnS₂ monolayer through the T_{S1} site is −3.98 eV, much higher than the cohesive energy of the Ru atom (0.85 eV). Moreover, it is also larger than the E_b in the T_{Sn} site of 3.64 eV and in the T_{S2} site of 2.85 eV. These findings mean that Ru doping on the SnS₂ monolayer through the T_{S1} site is quite thermodynamically favorable. After doping, the Ru adatom is captured by the surrounding S atoms, forming Ru–S bonds accordingly with a uniform bond length of 2.24 Å, slightly shorter than the sum of covalent radii of Ru and S atoms.²⁸ This finding manifests the strong binding force in the Ru–S bond with high chemical stability. In Figure 1b, one can see that the Ru dopant is surrounded by electron depletion, indicating its electron-donating behavior, in agreement with the Hirshfeld analysis that indicates that 0.223e transfers from the Ru dopant to the SnS₂ monolayer. On the other hand, the electron accumulation is mainly localized on the SnS₂ monolayer and the Ru–S bonds, suggesting the strong electron hybridization between the Ru dopant and S atoms.

To further confirm the chemical stability of a single Ru atom on the SnS₂ monolayer, the diffusion of the Ru atom from the T_{S1} site to the T_{S2} site is investigated. As shown in Figure 2, the energy barrier for Ru diffusion is as large as 4.11 eV, much higher than that of the critical barrier of 0.91 eV for reaction to occur energy-favorably at room temperature.²⁹ Therefore, we believe that the single Ru atom could be stably adsorbed on

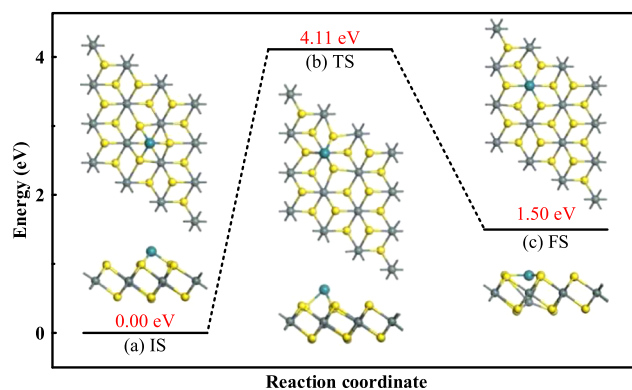


Figure 2. Ru atom diffusion on the SnS₂ monolayer: (a) initial state (IS) T_{S1} site, (b) transition state (TS), and (c) final state (FS) T_{S2} site.

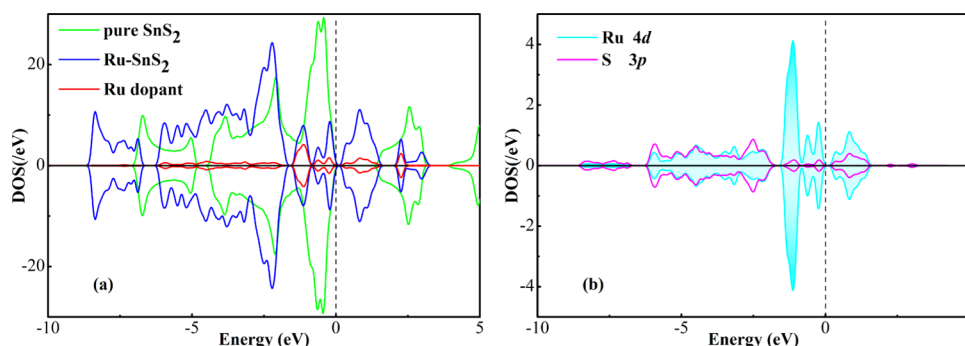


Figure 3. DOS of (a) pure and (b) Ru-doped SnS_2 systems. The dashed line indicates the Fermi level.

the SnS_2 monolayer through the T_{S1} site with a cluster-free problem.

After confirmation of the most stable configuration of the Ru– SnS_2 monolayer, its electronic behavior should be analyzed. Figure 3a plots the total density of state (DOS) of the pure and Ru-doped SnS_2 monolayer. One can see that pure SnS_2 monolayer performs semiconducting property without magnetic behavior. The band gap of the pristine SnS_2 monolayer is calculated as 1.56 eV based on its band structure (not shown here), close to the reported one of 1.61 eV based on generalized gradient approximation (GGA) calculations,³⁰ indicating the accuracy of our work. While after Ru doping, the DOS is obviously left-shifted to a lower region by about 2 eV, which suggests the strong electron-donating property of the Ru adatom, leading to the n-doping of the Ru– SnS_2 system. At the same time, the states of the Ru dopant contribute largely to the whole DOS of the system, in which some novel states appear within the band gap of the pure SnS_2 system around the Fermi level. Therefore, the conductivity of the Ru– SnS_2 monolayer would be significantly reduced compared with that of the pure counterpart. From Figure 3b, it is seen that the Ru 4d orbital is highly overlapped by the S 3p, which manifests the strong orbital interaction between Ru and S atoms. These findings also explain the strong electron hybridization and binding force during the formation of the Ru–S bond.

Figure 4 exhibits the optimized molecular structure of three typical VOCs of lung cancer. Through analysis of bond length

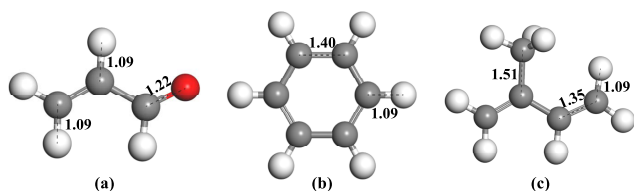


Figure 4. Molecular structures of (a) $\text{C}_3\text{H}_4\text{O}$, (b) C_6H_6 , and (c) C_5H_8 . The black values are bond lengths.

in different molecules, it is found that the C–H bond is measured as the same, while the C=O bond is longer than that of the C–H bond and the C=C bond is shorter than the C–C bond, indicating the stronger binding force for two C atoms in the double bond format. These results match well with the previous report.³¹

2.2. Adsorption of VOC Molecules. First, we initiate the analysis of the $\text{C}_3\text{H}_4\text{O}$ adsorption system, as displayed in Figure 5. We can find that the $\text{C}_3\text{H}_4\text{O}$ molecule prefers to be parallel to the Ru– SnS_2 surface on the top of the Ru dopant. However, the deformation of $\text{C}_3\text{H}_4\text{O}$ is evident after

adsorption, which is no longer a plane molecule on the Ru– SnS_2 monolayer, implying the geometric activation of the adsorbed gas molecules. Besides, one C atom is captured by the Ru dopant, forming a new Ru–C bond measured as 2.19 Å. That is, the Ru dopant exerts strong binding force upon the C atom of $\text{C}_3\text{H}_4\text{O}$, which therefore leads to the large E_{ad} of -1.42 eV. From the EDD, we find that electron accumulation is mainly localized on the gas molecule, while electron depletion is on the Ru– SnS_2 monolayer, manifesting the electron-withdrawing property of $\text{C}_3\text{H}_4\text{O}$ that agrees with the Hirshfeld analysis ($Q_{\text{T}} = -0.085e$). Besides, the Ru dopant is positively charged by 0.195e after adsorption. These results mean that 0.028e of the $\text{C}_3\text{H}_4\text{O}$ molecule are accepted from the Ru dopant, whereas 0.057e are from the SnS_2 surface. In other words, Ru bridges the charge transfer from the gas molecule to the SnS_2 layer, thus facilitating electron redistribution in the adsorbed system. Overall, based on all of these findings, we identify the $\text{C}_3\text{H}_4\text{O}$ adsorption on the Ru– SnS_2 surface as chemisorption.

As for the C_6H_6 adsorption in Figure 6, one can see that the most stable configuration is similar to that of the $\text{C}_3\text{H}_4\text{O}$ system, in which the C_6H_6 molecule is parallel with the SnS_2 layer right on top of the Ru dopant. After adsorption, the C_6H_6 molecule is slightly deformed, making the molecule a little bend toward the Ru dopant. This finding manifests the strong binding force between the Ru dopant and C_6H_6 molecule, as further confirmed by the large E_{ad} of -2.07 eV. Based on the Hirshfeld method, the Ru is positively charged by 0.218e and the C_6H_6 molecule is positively charged by 0.212e after the interaction. In other words, the Ru dopant behaves as an electron bridge, enhancing the charge transfer between the Ru– SnS_2 monolayer and the gas molecule, which is similar to that in the $\text{C}_3\text{H}_4\text{O}$ system. After Ru doping, the charge transfer can be remarkably intensified due to the large electron mobility and chemical reactivity of the Ru dopant, which therefore results in larger E_{ad} . From the EDD, one can see that electron accumulation is mainly localized on the Ru– SnS_2 monolayer, while electron depletion is mainly localized on the C_6H_6 molecule, which is consistent with the Hirshfeld analysis. Apart from that, the overlap of electron accumulation and electron depletion at the area between the Ru– SnS_2 layer and C_6H_6 molecule manifests the electron hybridization between two interaction species, which further verifies the strong adsorption performance of the Ru– SnS_2 monolayer toward the C_6H_6 molecule.

When it comes to the C_5H_8 system, the most stable configuration and the related EDD are depicted in Figure 7. It could be found that C_5H_8 prefers to be adsorbed on the Ru– SnS_2 surface through the molecule-parallel position with a

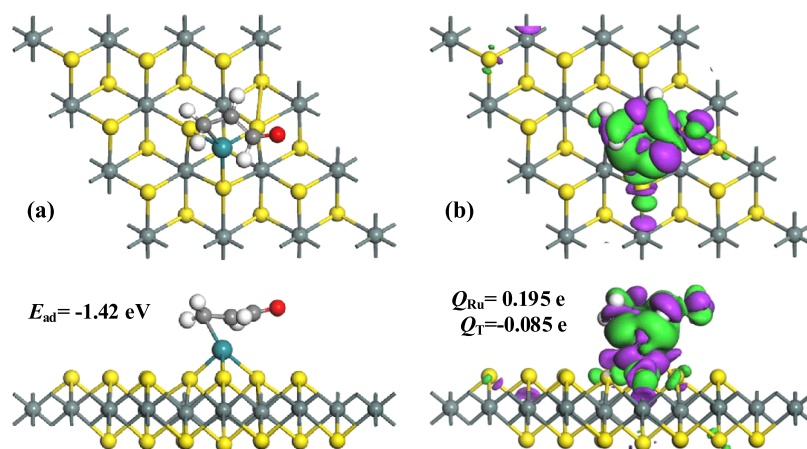


Figure 5. Adsorption configuration of the C_3H_4O system (a) and EDD (b). In EDD, the rosy areas indicate electron accumulation and the green areas indicate electron depletion; the isosurface is set to $0.008 \text{ e}/\text{\AA}^3$.

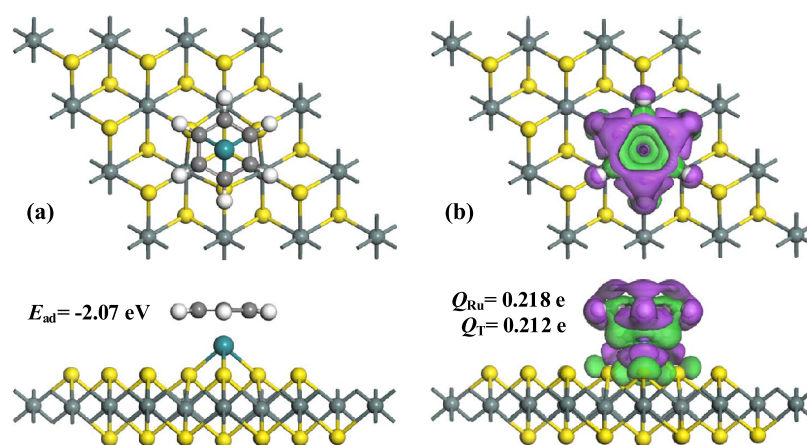


Figure 6. Adsorption configuration of the C_6H_6 system (a) and EDD (b). In EDD, the rosy areas indicate electron accumulation and the green areas indicate electron depletion; the isosurface is set to $0.008 \text{ e}/\text{\AA}^3$.

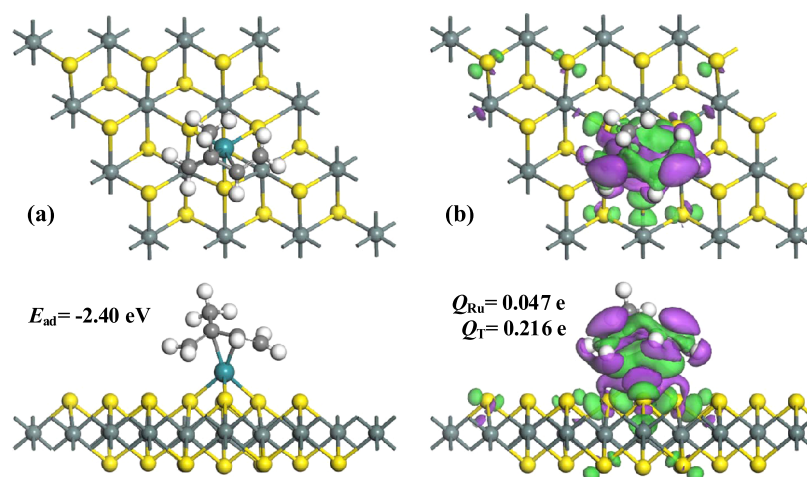


Figure 7. Adsorption configuration of the C_5H_8 system (a) and EDD (b). In EDD, the rosy areas indicate electron accumulation and the green areas indicate electron depletion; the isosurface is set to $0.008 \text{ e}/\text{\AA}^3$.

small slope to the plane. Rather than the little deformation of the C_6H_2 molecule after adsorption, the C_5H_8 molecule is afflicted with dramatic decomposition after being trapped by the Ru dopant with the formation of two Ru–C bonds. Originally, the five C atoms in the C_5H_8 molecule are in a same plane. However, after adsorption, the C atoms approach the Ru

dopant, making the molecule bend accordingly. Specifically, the C–C and C=C bonds becomes elongated to 1.53 and 1.41 Å on the Ru–SnS₂ surface and the newly formed Ru–C bonds are measured to be 2.15 and 2.17 Å, respectively. These results indicate not only the strong activation of C_5H_8 during adsorption³² but also the strong binding force between the Ru

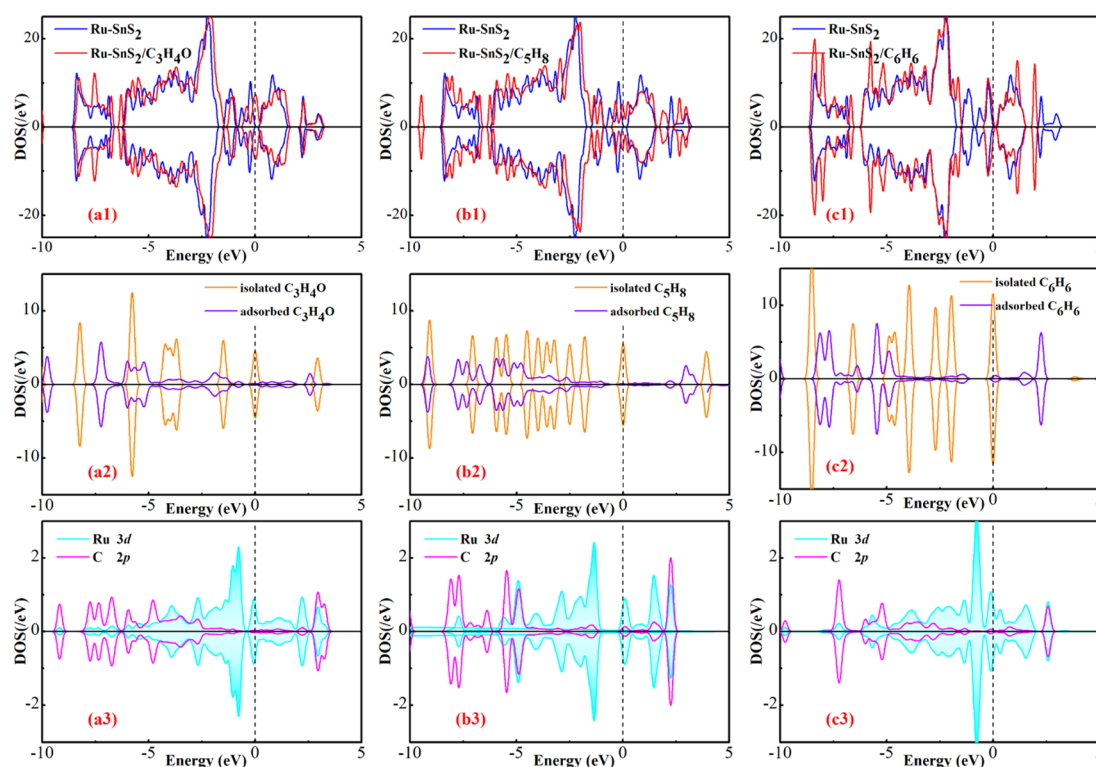


Figure 8. DOS in various adsorption systems: (a) $\text{C}_3\text{H}_4\text{O}$, (b) C_5H_8 , and (c) C_6H_6 .

dopant and C_5H_8 molecule. Combined with the calculated E_{ad} of -2.40 eV, chemisorption nature in this system could be identified. Besides, according to the Hirshfeld analysis, the C_5H_8 molecule as a whole transfers $0.216e$ to the Ru– SnS_2 surface, while the Ru dopant is positively charged by $0.047e$. That is to say, the Ru dopant behaves as an electron acceptor, withdrawing $0.176e$ from the C_5H_8 molecule and only $0.040e$ are accepted by the SnS_2 monolayer. From the EDD, one can observe that electron accumulation is mainly around the Ru center and electron depletion is mainly located on the C_5H_8 molecule. Considering the large charge transfer between the C_5H_8 molecule and Ru– SnS_2 monolayer, we presume that the ionic-bonding nature dominates the formation of Ru–C bonds in this system,³³ as supported by the overlap of electron accumulation and electron depletion on the Ru–C bonds, which indicates electron hybridization during their formation.

In short, the Ru– SnS_2 monolayer possesses the strongest interaction with the C_5H_8 molecule, followed by the C_6H_6 molecule and the last being the $\text{C}_3\text{H}_4\text{O}$ molecule. Besides, strong chemisorption is determined in three systems. At the same time, the electron hybridization could also be identified through EDD analysis, which verifies the orbital interaction in these systems. In addition, it is worth noting that when the results of charge transfer based on the Hirshfeld method are compared with Mulliken population the values are a little smaller with the same trend, but we assume that it would be more reliable because the Hirshfeld method does not rely on the basis set of the calculations. Thus, the electronic property of the Ru– SnS_2 monolayer is supposed to be changed due to gas adsorption, which will be analyzed in the next section.

2.3. DOS of the Ru– SnS_2 Monolayer upon Gas Adsorption. Figure 8 exhibits the total DOS and molecular DOS before and after gas adsorption, as well as the atomic DOS of bonding atoms to comprehensively understand the

electronic behavior of the Ru– SnS_2 monolayer for gas adsorption. It is seen from the total DOS that after adsorption the states of the Ru– SnS_2 monolayer undergoes a different level of deformation, which is attributed to the DOS states of the adsorbed gas molecules whose states are activated to some extent. Specifically, one can see that the DOS peaks of three isolated gases split into several small peaks near the Fermi level. In that case, the electronic behavior of the gas adsorbed systems would be remarkably impacted because of the contribution of the adsorbed gas molecules around the Fermi level. On the other hand, although there are some states located at the deep valence band, we assume that they have little effect on the electronic behavior of the whole system due to their weak activation.

Moreover, from the atomic DOS of Ru and C atoms, it is found that the Ru $4d$ orbital is highly overlapped by the C $2p$ orbital, ranging from -5 to 3 eV for the $\text{C}_3\text{H}_4\text{O}$ system and from -5 to 2.5 eV for C_5H_8 and C_6H_6 systems. These findings illustrate the strong electron hybridization and binding force of the Ru–C bond; this is in agreement with the previous EDD analysis. It is worth noting that the significant changes in the electronic behavior of the Ru– SnS_2 monolayer will accordingly change its electrical conductivity after adsorption. Based on this evidence, the sensing mechanism of a resistance-type sensor for detecting typical gases of lung cancer could be explored.

2.4. Frontier Molecular Orbital Theory Analysis. To explore the possibility of the Ru– SnS_2 monolayer as a resistance-type gas sensor for detecting typical gases of lung cancer, we, in this section, emphasize the analysis of frontier molecular orbitals to give an insight into the potential sensing mechanism of such a chemical gas sensor. Frontier molecular orbitals include highest molecular occupied orbital (HOMO) and lowest molecular unoccupied orbital (LUMO). It is well

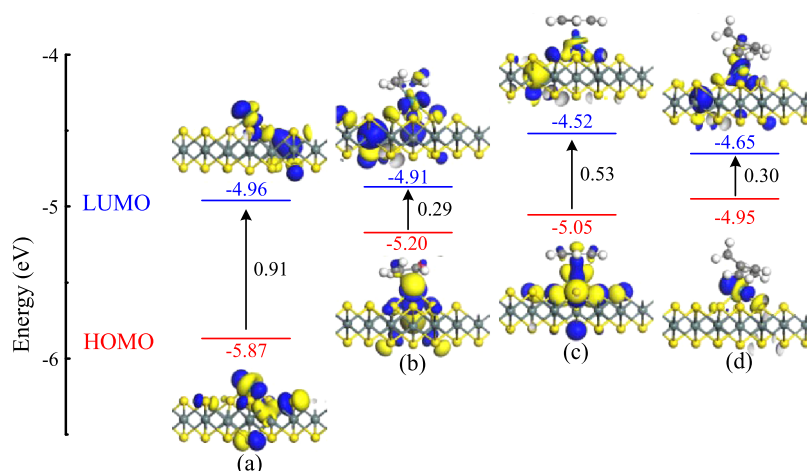


Figure 9. HOMO and LUMO distributions and E_g of different systems: (a) isolated Ru–SnS₂, (b) C₃H₄O system, (c) C₆H₆ system, and (d) C₅H₈ system.

known that the energy gap (E_g) between HOMO and LUMO is an effective parameter to evaluate the electrical conductivity of certain surfaces.^{34–36} Specifically, large E_g reveals small electrical conductivity and small E_g reveals large electrical conductivity.

Figure 9 exhibits the HOMO and LUMO distributions, their related energies, and the calculated E_g in various systems. It could be seen in the isolated Ru–SnS₂ system that HOMO and LUMO are all mainly located at the Ru dopant, while there also exist some HOMOs and LUMOs on the SnS₂ surface.

Besides, the energies of HOMO and LUMO for the Ru–SnS₂ monolayer are calculated to be -5.87 and -4.96 eV, respectively, and therefore, the E_g is 0.91 eV. This finding indicates its semiconducting behavior and manifests its suitability for gas sensing applications.³⁷

When it comes to the gas adsorbed systems, one can see that the HOMO and LUMO distributions of the Ru–SnS₂ monolayer experience pronounced changes. In the C₃H₄O system, one can see that HOMO is mainly around the Ru dopant and LUMO is localized on the SnS₂ layer, while there only has a few HOMOs and LUMOs on the C₃H₄O molecule; in the C₆H₆ system, the HOMO is mainly on the Ru dopant and in the area between the Ru adatom and C₆H₆ molecule, whereas the LUMO is largely localized on the Ru dopant; in the C₅H₈ system, the HOMO and LUMO are both mainly localized on the Ru dopant and a few are on the gas molecule. Along with these, changes in their distribution are the related changes in their energies and subsequently their E_g that finally determine the electrical conductivity of the system. Detailedly, the E_g in the C₃H₄O system declines to 0.29 eV; in the C₆H₆ system, it declines to 0.53 eV; and in the C₅H₈ system, it declines to 0.30 eV. As mentioned, the reduced E_g would result in an increase in conductivity of the Ru–SnS₂ monolayer after the adsorption of three typical gases. Moreover, the significant change in E_g will lead to evident changes in electrical conductivity. In this regard, we assume that the Ru–SnS₂ monolayer is a promising candidate for C₃H₄O, C₆H₆, and C₅H₈ sensing given the admirable change in its E_g after their adsorption. Moreover, for exhaled gas analysis, using a Ru–SnS₂-based gas sensor can realize an effective detection and as a result make an accurate diagnosis for possible lung cancer.

2.5. Recovery Property. To further characterize the possible use of the Ru–SnS₂ monolayer as a chemical sensor for lung cancer diagnosis, the recovery property is analyzed to determine the reusability of the typical sensor. The recovery behavior is the required minimum time for a sensor to desorb the adsorbed gases from its surface, in which the recovery time (τ) is explained by the transition state theory and the van't Hoff–Arrhenius expression³⁸

$$\tau = A^{-1} e^{(-E_a/K_B T)} \quad (1)$$

where A is the attempt frequency defined as 10^{12} s^{-1} ,^{39,40} T is the temperature, and K_B is the Boltzmann constant ($8.318 \times 10^{-3} \text{ kJ}/(\text{mol} \cdot \text{K})$). Also, the E_a (potential barrier) of desorption is equal to the value of E_{ad} due to the inverse process between the adsorption and desorption. It could be deduced that a larger E_{ad} would increase the difficulty for gas desorption and a temperature increase can accelerate that process largely. Based on our calculated E_{ad} in this work, however, the recovery time for such three typical gases of lung cancer from Ru–SnS₂ surface would be too long and even unrealistic at room temperature. On the other hand, when the temperature is higher than 600 K , the desorption becomes possible in one day. Considering the heat loss and the sanitary safety of the devices, we recommend the one-off operation of the gas sensors for the diagnosis of lung cancer. From this aspect, it is hopeful that Ru–SnS₂-based gas sensors with high sensitivity for typical gases of lung cancer could be further explored in the laboratory to extend their applications in the field of clinical medicine.

3. CONCLUSIONS

Using DFT, we theoretically investigated the Ru doping behavior on the SnS₂ monolayer and simulated the adsorption behavior of Ru–SnS₂ for three typical gases of lung cancer to explore its potential as a resistance-type sensor for lung cancer diagnosis. The main conclusions are as follows:

- A single Ru atom could be stably doped on the SnS₂ monolayer with high chemical stability and strong binding force without a cluster problem.
- The Ru–SnS₂ monolayer possesses high chemisorption of three gases that brings a significant change in its electronic property.

- (iii) After adsorption of typical gases of lung cancer, the conductivity of the Ru–SnS₂ monolayer could be increased, which provides the possibility for its exploration as biosensors for the diagnosis of lung cancer at an early stage.

Based on these, we suggest to explore Ru–SnS₂ as a resistance-type gas sensor in the clinical medicine. We are hopeful that our calculation could provide some guidance for its further exploration in other fields as well.

4. COMPUTATIONAL DETAILS

The DFT calculations were completed in the D mol³ package⁴¹ in a spin-polarized manner. To deal with the electron exchange–correlation terms, the Perdew–Burke–Ernzerhof (PBE) function with generalized gradient approximation (GGA) was considered.⁴² The DFT-D2 method was adopted to understand the Van der Waals force and long-range interactions, as proposed by Grimme.⁴³ Double numerical plus polarization (DNP) was selected as the atomic orbital basis set,⁴⁴ and the energy tolerance accuracy, maximum force, and displacement were determined as 10^{−5} Ha, 2 × 10^{−3} Ha/Å, and 5 × 10^{−3} Å,⁴⁵ respectively. The Brillouin zone Monkhorst–Pack grid was sampled with a *k*-point mesh of 5 × 5 × 1 for the supercell geometric optimizations and of 10 × 10 × 1 for related electronic calculations.⁴⁶ For static electronic structure calculations, a self-consistent loop energy of 10^{−6} Ha, a global orbital cutoff radius of 5.0 Å, and a smearing of 0.005 Ha were determined to ensure the accurate results of the total energy.⁴⁷

A 3 × 3 supercell containing 16 Sn atoms and 18 S atoms was established as the SnS₂ monolayer, on which one Ru atom was adsorbed to form the Ru–SnS₂ monolayer. The lattice constants of the pristine and Ru-doped SnS₂ monolayer were both calculated as 3.7 Å, in line with the previous report.¹⁹ For gas adsorption, the vacuum layer of 15 Å was used to prevent the interaction between adjacent units.⁴⁸ The adsorption energy (*E*_{ad}) is introduced to evaluate the interaction strength of adsorbing processes, calculated by the formula $E_{ad} = E_{surf/gas} - E_{surf} - E_{gas}$. In this formula, *E*_{surf/gas}, *E*_{surf}, and *E*_{gas} represent the energies of the gas adsorbed system, the pure Ru–SnS₂ surface, and pure gas species, respectively. In the meanwhile, Hirshfeld analysis was considered for charge transfer (*Q*_T) during gas adsorptions. The positive *Q*_T means the electron-donating behavior of the adsorbed gas molecule, while the negative *Q*_T indicates the electron-accepting behavior of the adsorbed gas molecule.

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Notes

The authors declare no competing financial interest.

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